

Fundamental Geochemical Processes Between CO₂, Water and Minerals

by

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Summary

The generic geochemical effects of adding CO₂ to water, to water and solids (with carbonate minerals) and to water and solids with exchangeable surface sites has been calculated and reviewed below. Although the reaction details are clearly a function of the fluid composition, the partial pressure of the CO₂ being added, the mineralogy and the cation exchange capacity, some generic conclusions can be reached. The atmosphere controls the final dissolved CO₂ levels and brings them back to very near original values – effectively, there is little or no carbon storage in the fluid. There is no carbon storage by precipitation of carbonate minerals in “short term processes – this process is driven by the dissolution of silicate minerals which react much more slowly. If carbonate minerals were present in the original mineralogy, some portion will dissolve (when CO₂ is added). This may result in additional CO₂ being released to the atmosphere.

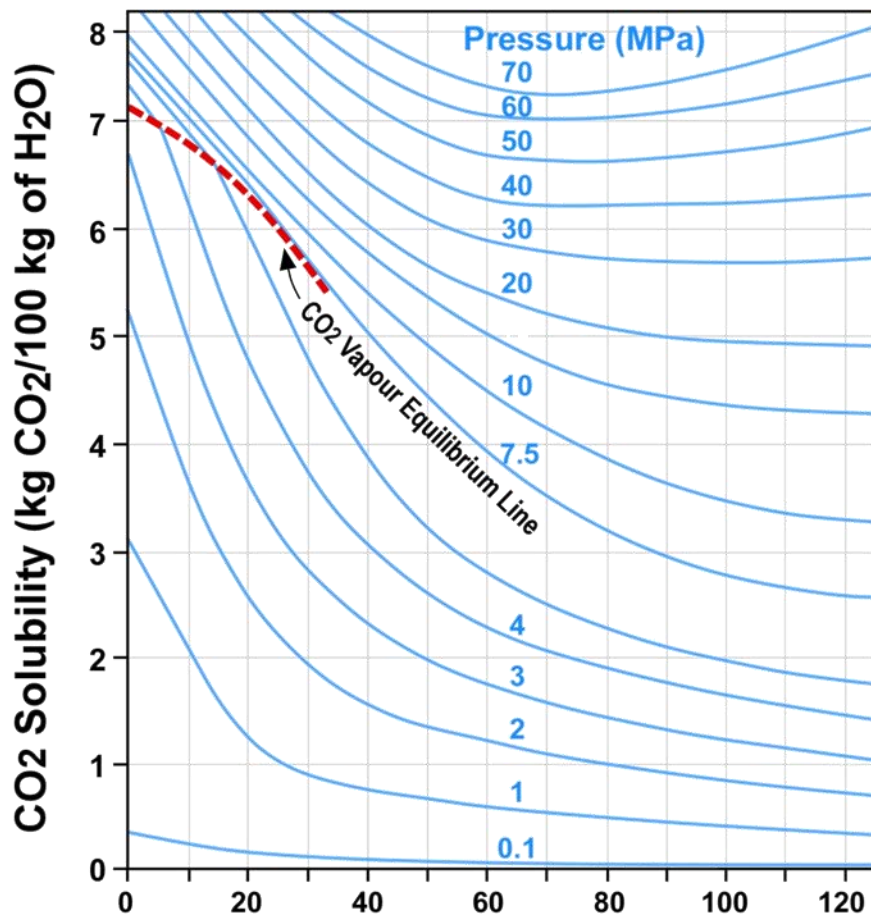
Fundamental Geochemical Processes

The solubility of carbon dioxide in pure water is a function of pressure and temperature, as shown in Figure 1. To summarize, increasing CO₂ pressure increases the solubility of CO₂ in the fluid. Increasing temperature decreases the solubility of CO₂ in the fluid unless the pressure and temperature is approximately above 30 MPa and 65 °C respectively, where solubility begins to increase.

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Figure 1: Solubility of CO₂ in pure water as a function of Temperature (deg C) (abscissa) and Pressure of CO₂ (MPa) (contours).

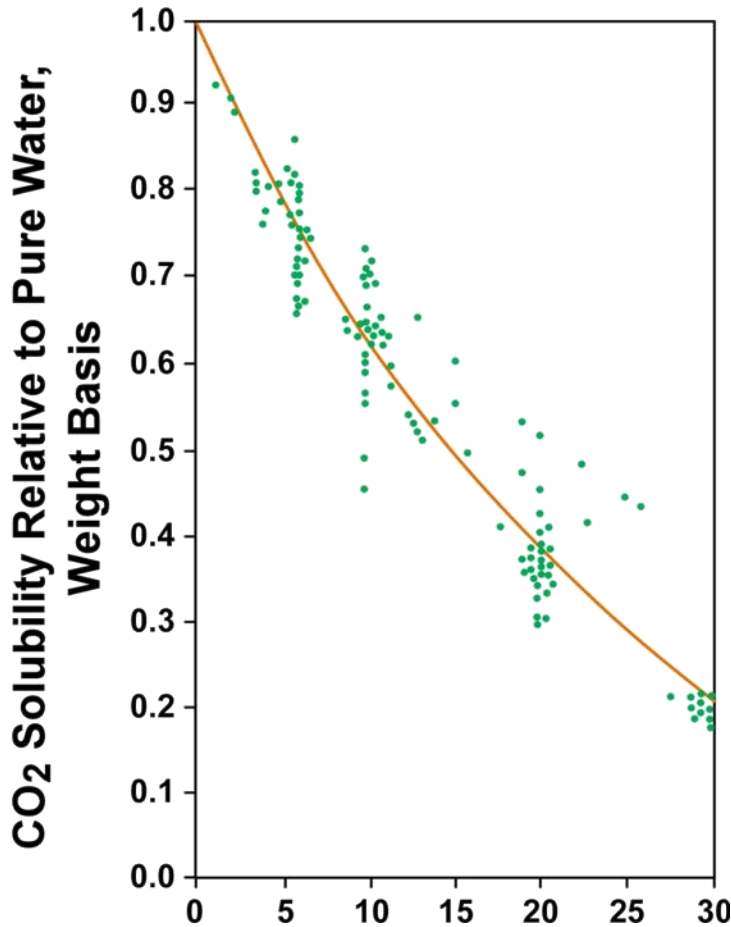


For reference, the molecular weight of CO₂ is about 0.044 kilograms / mole. At ambient conditions (25 °C, 1 bar total CO₂ pressure), the maximum solubility is in the order of several moles.

The solubility of CO₂ decreases as the amount of dissolved material in the water composition increases, as shown in Figure 2. The points on the graph show the range of values for different pressures and temperatures, and for fluid type. Fluid type refers to the dominate cation(s) and anion(s) in the fluid. For example, CO₂ solubility in sodium bicarbonate brines is different than in sodium chloride brines.

For reference: Sea water has about 35,000 to 36,000 mg/l dissolved solids (about 3 ½ weight percent solids). Formation waters in the Alberta Basin range from nearly fresh water (5,000 mg/l, or even more dilute) to salt saturation (~350,000 mg/l) although the basin average is about 46,000 mg/l.

Figure 2: Ratio of CO₂ dissolved in brine divided by CO₂ dissolved in pure water (ordinate) as a function of weight percent dissolved solids (abscissa). The points show the variation due to temperature and pressure.



As can be seen from Figure 2, the salting out effect (decrease in CO₂ solubility) due to total dissolved solids in a dilute fluid (say under 1000 mg/l TDS) would be relatively small.

CO₂ dissolved in water exists primarily as three different ions, carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻) and carbonate ion (CO₃⁼). Depending on the presence of other constituents, other ions which contain inorganic carbon may be present. Some common dissolved aqueous species that also contain inorganic carbon are NaCO₃⁻, NaHCO₃⁰, Na₂CO₃, MgCO₃, MgHCO₃⁺, etc. Except for unusual conditions like very high ionic strength brines, their concentrations are much lower than the three dominate carbonate ions. Thus they are rarely included in simple calculations. However, any reasonably sophisticated computer program includes their effect when the analytical data for the other components exist.

The relationships that describe the relative concentrations of the carbonate ions are a mass action equation and two mass balance equations. They are:

$$\text{Total Dissolved Carbon} = m(\text{H}_2\text{CO}_3) + m(\text{HCO}_3^-) + m(\text{CO}_3^{=})$$

$$\log K_1 = \log a(\text{H}_2\text{CO}_3) - \log a(\text{H}^+) - \log m(\text{HCO}_3^-)$$

$$\log K_2 = \log a(\text{HCO}_3^-) - \log a(\text{H}^+) - \log m(\text{CO}_3^{=})$$

where Total Dissolved Carbon is determined analytically, $\log K_1$ and $\log K_2$ are the appropriate log equilibrium constants for the equilibrium (obtained from tables or calculated), m and a are the molality and activity of the aqueous species respectively. If some or all of the previously mentioned “inorganic carbon bearing” aqueous species were to be included, then their molalities would be included in the “Total Dissolved Carbon” summation and mass balance equations for each of the species (similar in form to the two shown above) would be included.

Activity and molality are related for each individual species through the equation:

$$a = \gamma m$$

where γ is the activity coefficient (calculated) for that particular ion. Because of the presence of both normal (mass balance - the total dissolved carbon equation) and logarithmic equations (the mass action equations), iterative techniques must be used to solve these equations. It should be noted that the above equations are normalized to one kilogram of water. To obtain the total mass of any dissolved constituent, the molalities must be multiplied by the total mass of water.

The relationship between the partial pressure of CO_2 gas and dissolved carbon in solution is described by the following relationship:

$$\log K_3 = \log p(\text{CO}_2) + \log a(\text{H}_2\text{O}) - \log a(\text{H}_2\text{CO}_3)$$

Rigorously, the above equation should include the fugacity of CO_2 rather than the pressure. However, inclusion of the necessary equations to calculate the fugacity coefficient is beyond the scope of this department. For practical purposes, the pressure and fugacity are often considered the same. The activity of water is very near one (the log activity is very near zero) thus is often eliminated from the above equation.

Given enough time and surface area between a gas and a fluid, the partial pressure of CO_2 in a gas phase will equal the calculated partial pressure of CO_2 in the fluid phase. If the CO_2 partial pressure in the gas increases, CO_2 will dissolve into the fluid. If the CO_2 partial pressure in the gas decreases, then CO_2 will evolve from the fluid.

An immediate effect of evolving CO_2 from the fluid is to make the fluid more alkaline; if CO_2 dissolves into the fluid, then the fluid becomes more acidic. As discussed below, this can result in the dissolution (or precipitation) of solids, particularly carbonate minerals. This can be more easily seen if the above mass action equation is re-written to involve hydrogen ion:

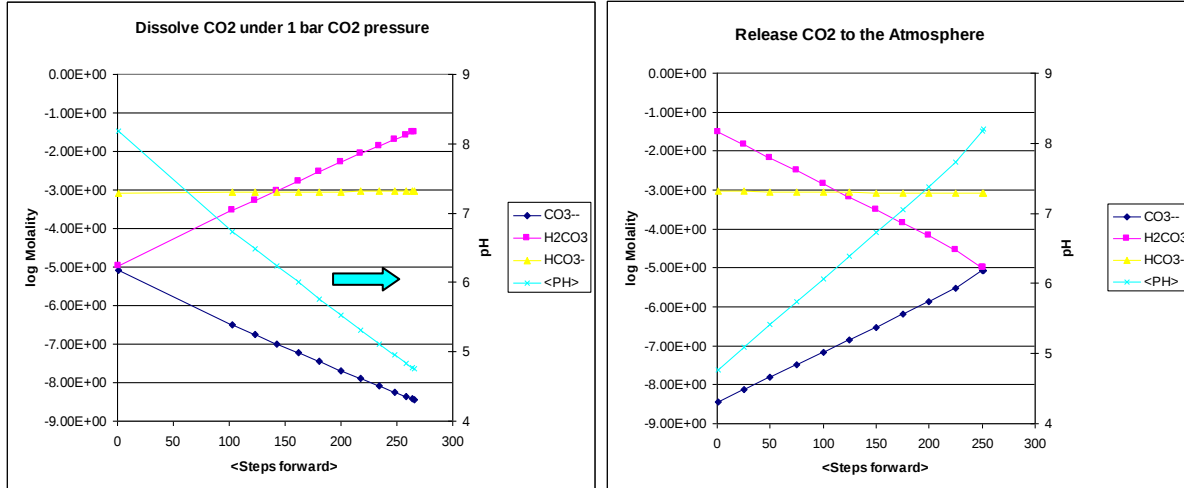
$$\log K_4 = \log p(\text{CO}_2) + \log a(\text{H}_2\text{O}) - \log a(\text{HCO}_3^-) - \log a(\text{H}^+)$$

or re-ordering the equation:

$$\log p(\text{CO}_2) = \log a(\text{HCO}_3^-) + \log a(\text{H}^+) - \log a(\text{H}_2\text{O}) - \log K_4$$

pH is defined as

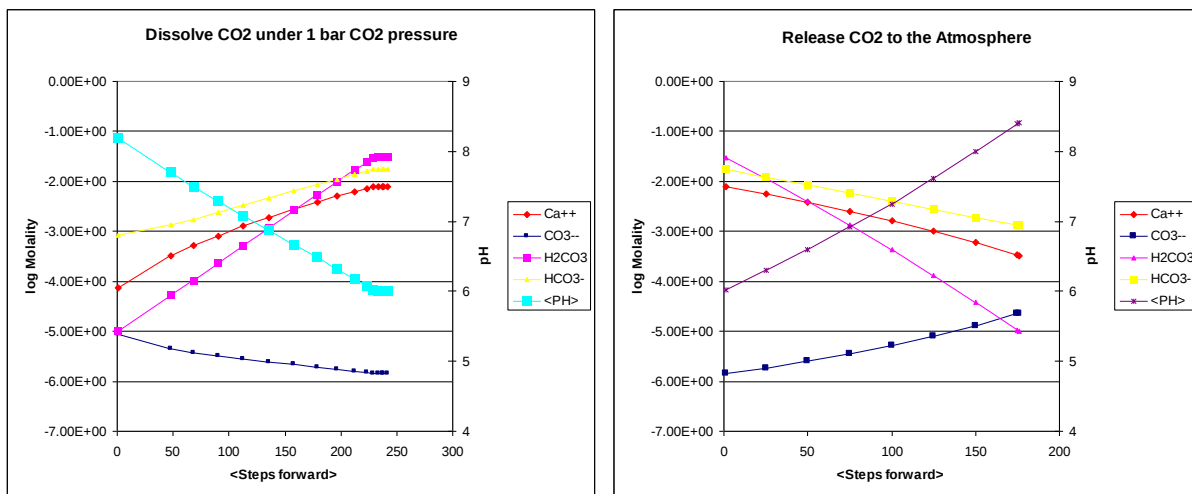
$$\text{pH} = -\log a(\text{H}^+)$$



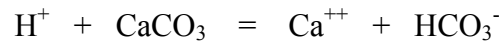
The effect of this processes are illustrated in the preceding two graphs. The graph on the left illustrates the change in the carbonate ions and pH as the fluid reacts with a CO₂ gas with 1 bar partial pressure, while the graph on the left shows the results when the final solution from the first is depressurize to the atmosphere.

For all practical purposes, the all of the CO₂ added during the 1 bar CO₂ pressurization is released back to the atmosphere. It is important to note that the concentration the bicarbonate is essentially constant through both processes and that the carbonate ion is present at lower concentrations the entire time. Thus, the change in alkalinity during these processes is zero or small if there are pH buffering reactions present in the fluid.

The following figures were calculated under the same conditions as the previous figures, except that the mineral calcite was presumed to be present and reactive. All other conditions were identical.

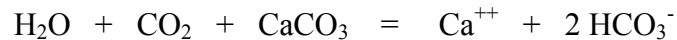


The effect of the dissolution of Calcite can be shown by the following equilibria between Calcite, CO₂, bicarbonate ion and hydrogen ion:



This equation show that if the fluid becomes more acidic, calcite will dissolve, and if fluid becomes more alkaline, calcite will precipitate. The effect is to buffer the change in pH.

If CO₂ is considered in the equilibria, then the following equilibria describes the process:

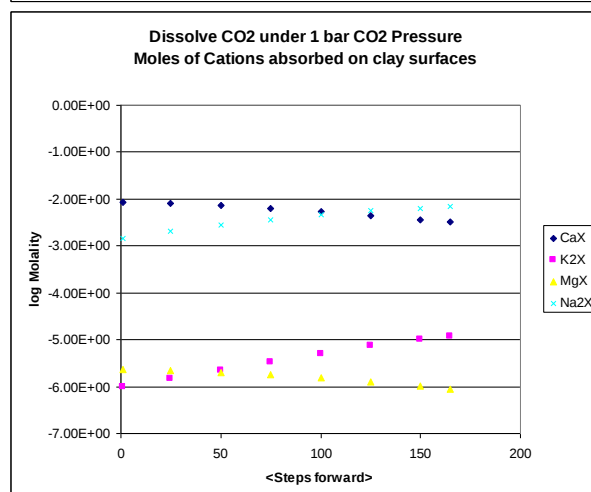
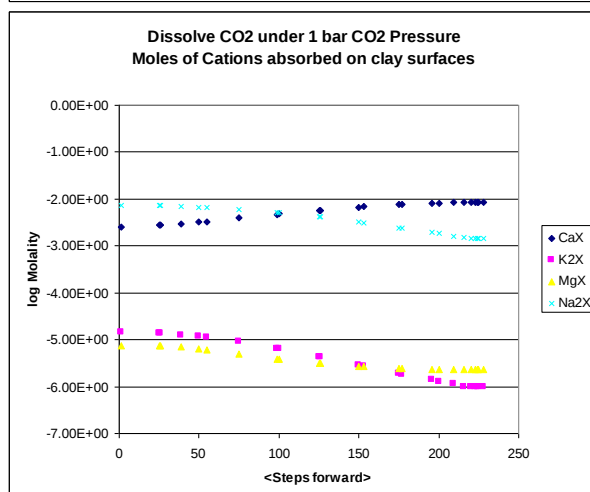
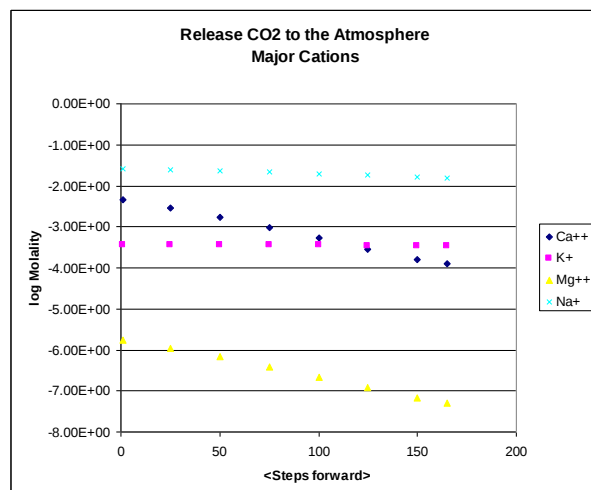
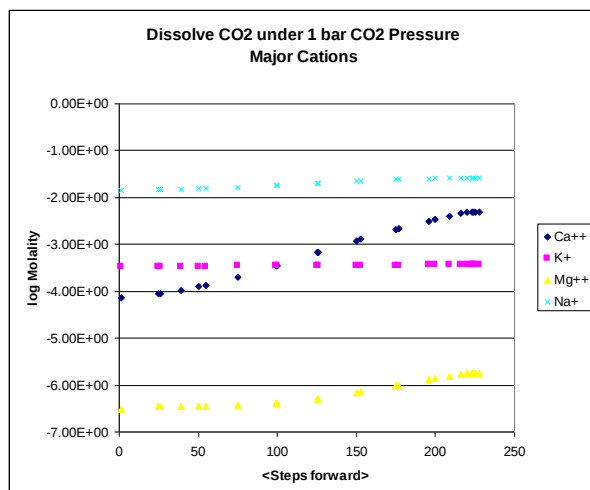
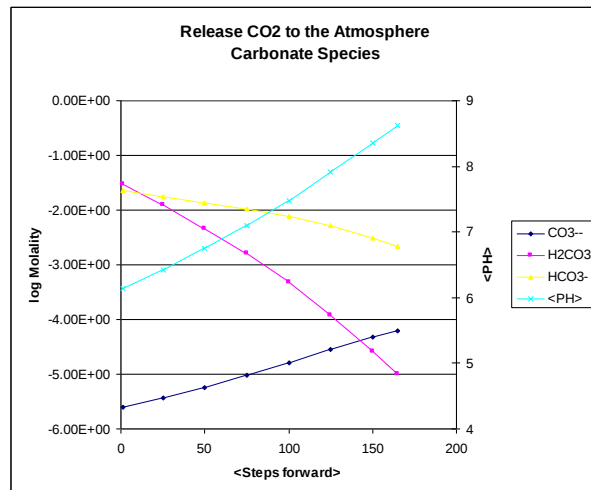
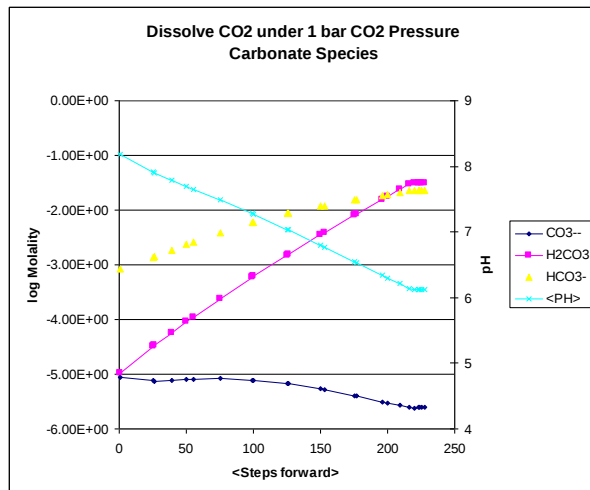


This equation shows that if CO₂ partial pressure increases with all else being equal, calcite will dissolve. If CO₂ partial pressure decreases, then calcite will dissolve.

In the preceding calculations, Calcite dissolved into the water due to the change in pH caused by the dissolution of CO₂ under 1 bar pressure. This has resulted in an increase in the calcium concentration. However, the dissolution of calcite has buffered the pH so the solution does not become as acidic as previous examples. This will result in slightly more CO₂ being dissolved in to the water.

Upon degassing to the atmosphere, Calcite precipitates and the pH returns to initial conditions. Because the relative rates of CO₂ degassing and calcite precipitation were not quite exactly the same under both case (due the use of a restart file), the final conditions are a little different than the initial cases.

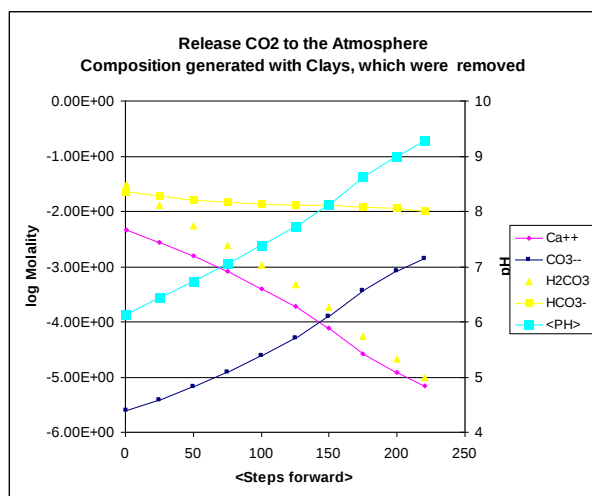
Ion exchange on surfaces can be a major constraint on fluid chemistry during reactions with solid phases, especially when significant amounts of clays are present. The following example shows how the presence of clays can affect the chemistry during CO₂ processes. In this example the presence of clays with approximately 10 milli-equivalents cation exchange capacity has been assumed. The ratio of the initially absorbed cations is assumed to be in equilibrium with the initial fluid. The remainder of the input is the same as the previous examples.



The effect of having 10 milli-equivalents of exchangeable surface area in this process does affect the computed results. There are measurable changes in the concentration of the major cations because the increased calcium in solution forces other cations off of the clay surfaces. As

per the previous example, calcite dissolution and precipitation are a significant impact on the system.

The degassing portion of the above calculations (which considered the effects of ion exchange) were undertaken in the presence of clays. If clay settle very fast relative to the degassing and precipitation, the effects of ion exchange are essentially removed. The following figure shows a simple simulation considering this effect.



The final pH is higher and the final calcium concentration is lower under these conditions, compared to the “ion exchange present” calculation. This is because calcite precipitation releases H⁺ while degassing consumes H⁺. In the clay absent during degassing calculation, the calcium which has been previously absorbed is not available for precipitation. Hence there is less buffering and the fluid becomes more alkaline.

The above calculations have been used to show the effects that would be expected during the absorption and de-absorption of CO₂ into / out of water. They are not an analysis of any laboratory data, nor are they representative of any surface mining operation, except by accident. They have been made using the geochemical modeling program, GAMSPath, with a standard database and assumed fluid and mineralogical data.

The above modeling were for relatively rapid geochemical processes at ambient (or near ambient) temperatures. Under these conditions, silicate minerals do not react appreciably because their reaction kinetics are much slower. Thus they do not impact the state of CO₂ in these calculations.

To accurately model the addition and/or release of CO₂ for any real world problem or to evaluate observed data, the following information should be available, either through direct measurement or approximation:

- Mineralogy: both the identity, mass and surface area. Carbonate minerals and clays must be identified.
- Initial fluid chemistry: analytical data.

- The cation exchange capacity (CEC) and the initial fraction of each component dissolved on the surface. This should be identified specific to each mineral.
- Temperature and total pressure.
- If a gas is present, the partial pressure of the gas components, particularly CO₂.

In the absence of a portion of the above data, the calculations be used to constrain interpretation or to make predictions, but their accuracy depends on good estimations of these parameters.

In conclusion, the above modeling allows the following observations to be made about the effects absorbing CO₂:

- The pH becomes more acidic.
- The total dissolved inorganic carbon (TIC) increases. If calcite or buffering reaction are not present, then a measured alkalinity will be constant.
- If calcite is present, it will dissolve. This will allow slightly more CO₂ to be absorbed.
- If clays and calcite are present, more calcite will dissolve. Some of the additional calcium will absorb on the clay surfaces, thus increasing the concentrations of potassium, sodium and magnesium.

Based on the above modeling, there are two potential cases during the degassing which will occur on exposure to the atmosphere. If the original clays are present, then:

- The pH becomes more alkaline, and essentially equal to the original value.
- The total dissolved inorganic carbon (TIC) decreases to equilibrium with the atmosphere.
- Calcite will precipitate, bringing the calcium concentrations back to the initial levels. This will also decrease the absorbed calcium on the clay surfaces.

If the original clays have been removed before degassing occurs, then:

- The pH becomes more alkaline than the “clay present case”.
- The total dissolved inorganic carbon (TIC) decreases to equilibrium with the atmosphere. Because of the more alkaline pH, it will be greater than the “clay present case”.
- Calcite will precipitate (not as much as the “clay present case”) and the resulting calcium levels will be lower than the original values.

The exact values need to be calculated using the appropriate input values.

The most important effect of the atmosphere is to bring the total dissolved inorganic carbon levels back to very near original values by fluid degassing – effectively, there is little or no carbon storage in the fluid. When atmospheric buffering is present, then there is no carbon storage as carbonate minerals in the solids. If carbonate minerals were present in the original mineralogy, some portion will dissolve (when CO₂ is added) which may result in additional CO₂ being released to the atmosphere.